

# PATENT SPECIFICATION

(11) 1 518 060

1 518 060

- (21) Application No. 42550/76 (22) Filed 13 Oct. 1976  
 (31) Convention Application No. 7 531 828  
 (32) Filed 17 Oct. 1975  
 (31) Convention Application No. 7 628 248  
 (32) Filed 21 Sept. 1976 in  
 (33) France (FR)  
 (44) Complete Specification published 19 July 1978  
 (51) INT CL<sup>2</sup> C08G 69/44; D01F 6/78  
 (52) Index at acceptance

C3R 22A 22D1A2 22D1AX 22D2A2 22D2AX 22D3D1  
 22D3DX 22M6 22N1A 22N1B 22N2 22NX 22P1  
 22T2



## (54) COPOLYETHERESTERAMIDES AS ANTISTATIC FIBRES AND FILAMENTS

(71) We, ATO CHIMIE, a French Body Corporate, of Tour Aquitaine, 92400 Courbevoie, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

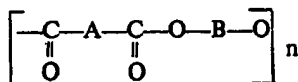
This invention relates to fibres and filaments possessing natural antistatic properties without the need to incorporate any additives in order to reduce or eliminate electrostatic charges caused by friction.

A number of compounds can be added to polymers to confer antistatic properties. For example, when a copolyether-esteramide is mixed with a polyamide (as described in French patent 2,178,205), the product resulting from moulding or extrusion of the mixtures possesses antistatic properties.

However, such a process means that the copolyetheresteramide also has to be prepared, in order to be added to the polyamide, to ensure satisfactory ohmic resistance in the resulting plastic material.

This invention overcomes these drawbacks. It concerns fibres and filaments consisting of a block copolyesteramide or copolyetheresteramide obtained by reaction of dicarboxylic linear aliphatic polyamide with a polyoxyalkylene glycol, which polyesteramide has itself antistatic properties without the need to add any extra substance to obtain such properties.

These fibres and filaments are made from macromolecular materials based on polyamides containing polyester or polyesterether units with the following structure:



where n is an integer indicating repetition of the group, A represents the polyamide block, preferably of the type 6, (e.g. a caprolactan polymer), 6—6, (e.g. an adipic acid/hexamethylene diamine copolymer), 6—10, (e.g. a sebacic acid/hexamethylene diamine copolymer), 11, (e.g. an amino-undecanoic acid polymer), or 12 (e.g. a dodecanolactan polymer), and the grouping O—B—O— represent a structure derived from an  $\alpha$ - $\omega$ -diol such as ethylene glycol, propylene glycol, 1-4-butane diol, 1-3-propane diol, 1-6 hexane diol, an oxy- or polyoxyalkylene glycol of low molecular weight obtained by dimerization, trimerization or oligomerization of C<sub>1</sub> to C<sub>4</sub>  $\alpha$ - $\omega$ -diols such as trioxyethylene glycol, tetraoxypropylene glycol or a polyoxyalkylene glycol of molecular weight no greater than 450. When  $\alpha$ - $\omega$ -diols without an etheroxide group inside the hydrocarbon chain, such as ethylene glycol or propylene glycol, are used, this results in a block copolyesteramide. When  $\alpha$ - $\omega$ -diols containing etheroxide groups in the chain, such as polyoxyethylene glycol, are used, this produces a block copolyether-esteramide. Block copolyetheresteramides of similar structure have been prepared, using the methods described in British patent No. 1,473,972, but these substances were intended mainly for moulded articles or extruded films and sheets, and did not necessarily possess the qualities required for antistatic fibres and filaments.

If the fibre or filament is to resist the phenomenon of electrostatic charging by friction, while retaining adequate technical properties, the plastic must be mainly polyamide-based, and the percentage weight of oxyalkylene or polyoxyalkylene sequences must be between 1 and 20%, an preferably between 3 and 15%.

The polyamide used is preferably a linear

45

50

55

60

65

70

75

80

85

aliphatic polyamide of the 6,6—6,6—10, 11, or 12-polyamide type, as exemplified above, with carboxylic groups at the chain-ends, obtained either by polymerizing a lactam or an amino acid in the presence of a small quantity of a dicarboxylic  $\alpha$ - $\omega$ -linear aliphatic acid, or else by reaction between a linear aliphatic  $\alpha$ - $\omega$ -diamine and a dicarboxylic  $\alpha$ - $\omega$ -linear acid, in the presence of excess linear aliphatic  $\alpha$ - $\omega$ -diacid, to create carboxylic chain-ends and act as a chain-limiter.

The quantity of linear  $\alpha$ - $\omega$ -diacid used therefore depends on the length and average molecular weight of the polyamide sequence required. The polyamide blocks have molecular weights of between 300 and 10,000, and preferably of about 2,000.

Suitable lactams include butyrolactam, caprolactam, decanolactam, undecanolactam and lauroilactam.

Suitable amino acids include 6-amino-hexanoic acid, 10-aminodecanoic acid, 11-aminoundecanoic acid, 12-amino-undecanoic acid.

Suitable linear aliphatic  $\alpha$ - $\omega$ -diamines include hexamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, dodecamethylenediamine, hexadecamethylenediamine, 1-20-diamino-eicosane, and 1-22-diamino-docosane.

Suitable linear aliphatic  $\alpha$ - $\omega$ -diacids include adipic, sebacic, azelaic, decanedioic, undecanedioic and dodecanedioic acids.

The reaction is performed by a standard process, involving heating of raw materials in a strong vacuum in the presence of a catalyst consisting of a tetra-alkyl-orthotitanate with the formula  $Ti(OR)_4$ .

The reaction temperature is above the melting points of the raw materials involved, and should be high enough to keep the reaction mixture fluid: between 100 and 400°C, and preferably between 200 and 300°C. The reaction may last between 10 minutes and 10 hours, and preferably between 1 and 7 hours: the duration depends on the degree of viscosity required for the involved copolyesteretheramide.

Reaction is performed in a strong vacuum, of approximately 0.5 to 5 mm Hg.

If the amount of  $\alpha$ - $\omega$ -diol or oxyalkylene glycol or polyoxylene glycol used is such that the percentage weight of such blocks is between 1 and 20%, and preferably 3 and 15% of the total weight of block polyesteramide or copolyetheresteramide produced, this will provide a copolyesteramide or copolyetheresteramide of high molecular weight, suitable for spinning of fibres and filaments which possess their own antistatic properties, and to which there is no need to add an antistatic compound, usually

required when preparing polyamide-based textile fibres.

Another advantage of these new copolyesteramide or copolyetheresteramide fibres and filaments resides in the fact that they keep their antistatic properties, whereas equivalent properties provided by an additive are known to wear off as time elapses and as the products are washed repeatedly.

These copolyetheresteramides or copolyesteramides are spun on a machine suitable for use with a small quantity of material, the melter temperature being 265°C, the nozzle temperature 255°C, and reeling speed 70 m per minute. The resulting fibres comprise 23 strands, not twisted.

The circular section of each filament is approximately 21 to 24 microns.

The resulting fibres are then cold-stretched at the rate of 4.8, with an unreeling speed of 35.4 m per minute and reeling speed of 170 m per minute. Fibres made from the materials above are spun without oiling treatment, whereas Rilsan (Registered Trade Mark — on 11 polyamide) is given such treatment.

Ohmic resistance measurements were performed on the basis of a 1-metre length of fibre, voltage of 400 V, temperature 20°C, and 65% relative humidity.

Viscosity measurements were carried out at 25°C in metacresol at a concentration of 0.5 g per 100 ml.

The invention is illustrated by, without being confined to, the following examples.

#### EXAMPLE 1.

300 g dicarboxylic 11-polyamide with an average molecular weight of 2090, obtained by polycondensation of 11-amino-undecanoic acid in the presence of adipic acid, was placed in a 1-litre reactor. 65 g dioxethylene glycol and 1 g tetrabutyl-orthotitanate were then added. The reaction mixture was heated in nitrogen to a temperature of 240°C. The reaction was continued under reflux at 250°C for four hours, the mixture being well-agitated in an inert atmosphere, after which the temperature was raised to 260°C and a vacuum was created inside the reactor to remove excess dioxethylene glycol. The reaction was continued at this temperature for 1 hour at an 0.1 mm Hg pressure.

The resulting product had the following properties:

— intrinsic viscosity 1.35

— melting point 173°C

— Glass transition point -16°C

The product contained 5% by weight of

- dioxyethylene glycol sequences in relation to the total mass.
- The product was ground and spun as described above.
- 5 The resulting fibres contained 23 strands, which were not twisted, of 4 deniers and with an average circular section of 23.98 microns.
- 10 Dynamometric tests were performed on these products using a Dynstron dynamometer with a tension-bar speed of 20 cm per minute and pretension of 0.5 centinewtons, with the following results:
- elongation at breaking point: 17.9%
  - 15 — rupture strength: 525 g
  - elastic modulus: 29.1 g/denier
  - grist: 4 denier
  - ohmic resistance per metre of fibre:  $7.14 \times 10^{12}$ .
  - 20 In comparison, the following results were obtained under the same experimental conditions for an 11-polyamide which had been treated with an additive to confer anti-static properties to it:
  - 25 — elongation at rupture point: 12.8
  - rupture strength: 527 g
  - elastic modulus: 48.2/g denier
  - grist: 3.4 denier
  - ohmic resistance per metre of fibre:  $4.46 \times 10^{13}$ .
- 30
- 35
- 40
- 45

#### EXAMPLE 2.

With the same procedure as in example 1, 209 g 11-dicarboxylic polyamide, obtained by polycondensation of 11-amino undecanoic acid in the presence of adipic acid and with a molecular weight of 2090, was made to react with 60 g trioxyethylene glycol, in excess in relation to the polyamide, and 1 g tetrabutylorthotitanate.

The resulting product had the following properties:

- intrinsic viscosity 1.3
- melting point 173°C
- Glass transition point -14°C

The product contained 7% weight of trioxyethylene glycol sequence in relation to the total mass. The product was spun in three batches. Table 1 below shows the properties of the fibres in these 3 batches.

TABLE 1

Batch	1	2	3
Grist of deniers	3.49	3.22	3.89
% Elongation at rupture point	17.3	16.3	16.1
Rupture strength in g	440	443	432
Elastic modulus in g/denier	14.1	—	17.2
Resistance in ohms/m fibre	$5.00 \times 10^{14}$	$5.71 \times 10^{14}$	$7.00 \times 10^{14}$

All these products have antistatic properties.

#### EXAMPLE 3.

- 55 Using the same procedure as the one described in example 1, 209 g 11-dicarboxylic polyamide, with a molecular weight of 2090, was made to react with 42.5 g polyoxyethylene glycol, with an average molecular weight of 425, and 1 g tetrabutyl-orthotitanate. This reaction mixture was placed in an inert atmosphere and heated to a temperature of 260°C. A vacuum was then created inside the reactor and the reaction continued, while the mixture was

stirred vigorously, at 260°C for 4 hours in an 0.1 mm Hg vacuum.

- intrinsic viscosity 1.4
- melting point 173°C
- Glass transition point -60°C

This product contained 17% weight of polyoxyalkylene glycol sequence in relation to the total mass. The product was spun in two batches. Table 2 shows the properties of the fibres in these two batches, containing 23 strands, not twisted.

65

70

75

Batch	1	2
Grist in deniers	3.75	3.12
Rupture strength in g	310	308
% elongation at rupture point	29.3	18.0
Elastic modulus in g/denier	13.5	15.1
Resistance in ohms/m fibre	4.89 $10^{12}$	5.82 $10^{12}$

#### ANTISTATIC PROPERTIES

If the results obtained in the first three examples as summarized in table 3 below are compared, it will be noted that the antistatic property expressed by the resistance in ohms per metre of fibre increases with the percentage weight of polyesterether sequence in the copolyesteretheramide. On the other hand, the elastic modulus in g per denier decreases in relation to the increased percentage weight of polyesterether

sequences. Antistatic properties are equivalent to those of 11-polyamide treated with an antistatic agent when the copolyesteretheramide contains 5 to 7% polyesterether sequences. It is better not to have more than 17% polyesterether sequences because of the reduced elastic modulus, since this reduction becomes greater as the percentage of polyesterether sequences increases.

TABLE 3

% weight of polyetherester sequence in the chain in relation to total mass	% weight of polyamide sequences	Physical Properties of Filaments					Antistatic properties expressed as resistance in ohms per metre of fibre
		No. of strands/filament	Average weight in microns	denier	Elastic modulus in g/denier		
(11-polyamide treated with an antistatic agent)	100%	23	21.17	3.40	48.2	4.46 · 10 <sup>12</sup>	
5%	95%	23	23.98	4.00	29.1	7.14 · 10 <sup>12</sup>	
7%	93%	23	21.67	3.49	14.1	5.00 · 10 <sup>14</sup>	
7%	93%	23	21.35	3.22	—	5.71 · 10 <sup>14</sup>	
7%	93%	23	21.92	3.89	17.2	7.00 · 10 <sup>14</sup>	
17%	83%	23	22.56	3.75	13.5	4.89 · 10 <sup>15</sup>	
17%		23	19.80	3.12	15.1	5.82 · 10 <sup>15</sup>	

**EXAMPLE 4.**

With the same procedure as in example 1, 300 g 11-dicarboxylic polyamide, with an average molecular weight of 2090, was made to react with 62 g ethylene glycol in excess of 1 g tetrabutyl orthotitanate. The reaction mixture was heated to 230°C, and this temperature was maintained for four hours while the mixture was agitated in an inert atmosphere. The temperature was then raised to 260°C, after excess glycol had been removed, after which a vacuum was created inside the reaction and the reaction continued at this temperature for one hour in an 0.1 mm Hg vacuum.

The resulting product had the following properties:

- intrinsic viscosity 1.4
- melting point 173°C
- Glass transition point -18°C

The product contained 3% weight of ethylene glycol sequences in relation to the total mass.

**EXAMPLE 5.**

1 kg 6-dicarboxylic polyamide with an average molecular weight of 2,000, obtained by polycondensation of caprolactam in the presence of adipic acid, was placed in a 6-litre stainless steel reactor. 170 g dioxethylene glycol and 3.5 g tetrabutyl orthotitanate were added.

The reaction mixture was heated in nitrogen to a temperature of 230°C, at which reaction continued by reflux for one hour, the mixture being well stirred in an inert atmosphere, after which the temperature was raised to 250°C and excess dioxethylene glycol was distilled in a vacuum of 0.1 mm Hg. The reaction continued under these conditions for one hour.

The resulting product had the following properties:

- intrinsic viscosity 1.3
- melting point 192°C

The product contained 5% weight of dioxethylene glycol sequence in relation to the total mass.

The product was ground cryogenically to produce a powder with a grain size of between 80 and 200 microns.

Resistivity in ohms per metre of fibre was  $6.1 \times 10^9$ .

**EXAMPLE 6.**

With the same procedure as in example 1, 1 kg 6-dicarboxylic polyamide with a molar

mass of 2,000 was made to react with 200 g trioxyethylene glycol and 4 g  $\text{Ti}(\text{OBU})_4$ .

The resulting product had the following properties:

- intrinsic viscosity 1.35
- melting point 192°C

The product contained 7% weight of trioxyethylene glycol sequence in relation to the total mass.

The resistivity in ohms per metre was  $3.5 \times 10^9$ .

**EXAMPLE 7.**

1 kg 6-dicarboxylic polyamide, with a molar mass of 2,000, was made to react in a 6-litre stainless steel reactor with 212 g polyoxyethylene glycol, with a molecular weight of 425, and 3.5 g  $\text{Ti}(\text{OBU})_4$ .

The reaction mixture was placed in an inert atmosphere and heated to a temperature of 260°C. A vacuum was then created inside the reactor and the reaction continued, while the mixture was well-stirred, at a temperature of 260°C for four hours in an 0.1 mm Hg vacuum.

The resulting product had the following properties:

- intrinsic viscosity 1.45
- melting point 192°C

The product contained 17% weight of polyoxyethylene glycol sequence in relation to the total mass.

The resistivity in ohms per metre was  $7.5 \times 10^8$ .

**EXAMPLE 8.**

1 kg 6-6-dicarboxylic polyamide, with a molar mass of 2,000, obtained by the polycondensation of hexamethylene adipamide in the presence of adipic acid, was made to react in 6-litre stainless steel reactor with 170 g dioxethylene glycol and 2.5 g  $\text{Ti}(\text{OBU})_4$ .

The reaction mixture was heated in nitrogen to a temperature of 270°C for four hours by glycol reflux, while being agitated. Excess glycol was distilled and polycondensation continued in an 0.5 mm Hg vacuum for one hour.

The resulting product had the following properties:

- intrinsic viscosity 1.25
- melting point 245°C

The product contained 5% weight of dioxethylene glycol sequence in relation to the total mass.

The resistivity in ohms per metre was  $1.6 \times 10^{10}$ .

#### EXAMPLE 9.

With the same procedure as in example 4, 1 kg 6-6-dicarboxylic polyamide, with a molar mass of 2,000, was made to react with 200 g trioxyethylene glycol and 4 g Ti (BuO)<sub>4</sub>.

The resulting product has the following properties:

— intrinsic viscosity 1.35

— melting point 245°C

The product contained 7% weight of trioxyethylene glycol sequence in relation to the total mass.

The resistivity in ohms per metre was  $4.4 \times 10^9$ .

#### EXAMPLE 10.

1 kg 6-6-dicarboxylic polyamide, with a molar mass of 2,000, was made to react in a 6-litre stainless steel reactor with 212 g polyoxyethylene glycol, with a molar mass of 425, and 3.5 g Ti(OBu)<sub>4</sub>.

The reaction mixture was placed in a nitrogen atmosphere and heated to a temperature of 270°C. The reaction continued in an 0.5 mm Hg vacuum, while the mixture was well agitated, for one hour at 265°C and for one hour at 285°C.

The resulting product had the following properties:

— intrinsic viscosity 1.4

— melting point 245°C

The product contained 15% weight of polyoxyethylene glycol sequence in relation to the total mass.

The resistivity in ohms per metre was  $1.2 \times 10^9$ .

#### WHAT WE CLAIM IS:—

1. Antistatic fibres and filaments formed from block linear aliphatic copolyester-

amides or copolyetheresteramides obtained by the reaction between a linear aliphatic polyamide block with a molecular weight of from 3000 to 10,000, and with carboxylic terminal groups and a linear aliphatic  $\alpha$ - $\omega$ -diol or polyoxyalkylene glycol with hydroxylated chain-ends, using tetra-alkyl-orthotitanate as catalyst, the percentage weight of diol residues in the polymer being from 1 to 20%.

2. Antistatic fibres and filaments as defined in Claim 1, in which the polyamide block is an 11-polyamide.

3. Antistatic fibres and filaments as described in Claim 1, in which the polyamide block is a 6-6-polyamide.

4. Antistatic fibres and filaments as defined in Claim 1, in which the polyamide block is a 6-6-polyamide.

5. Antistatic fibres and filaments as defined in any preceding Claim in which the  $\alpha$ - $\omega$ -diol is ethylene glycol.

6. Antistatic fibres and filaments as defined in any of Claims 1 to 4, in which the  $\alpha$ - $\omega$ -diol is dioxyethylene glycol.

7. Antistatic fibres and filaments as defined in any of Claims 1 to 4, in which the  $\alpha$ - $\omega$ -diol is trioxyethylene glycol.

8. Antistatic fibres and filaments as defined in any of Claims 1 to 4, in which the  $\alpha$ - $\omega$ -diol is a polyoxyethylene glycol of molecular weight not greater than 450.

9. Antistatic fibres and filaments according to any preceding Claim, wherein the molecular weight of the linear aliphatic polyamide block is 2000.

10. Antistatic fibres and filaments according to any preceding Claim, wherein the percentage weight of glycol or ester glycol residues is from 3 to 15%.

11. Antistatic fibres and filaments according to Claim 1 and substantially as herein described with reference to the Examples.

WITHERS & ROGERS,  
Chartered Patent Agents,  
148—150 Holborn,  
London, EC1N 2NT.  
Agents for the Applicants.